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| (54) Title: ALUMINUM-FREE MONOCYCLOPENTADIENYL METALLOCENE CATALYSTS FOR OLEFIN POLYM- ERIZATION (57) Abstract The invention is a catalyst system including a Group IV-B transition metal component and an activator component which may be employed to polymerize olefins to produce a high molecular weight polymer. The Group IV-B transition metal component contains a single cyclopentadienyl ligand and a single heteroatom ligand, which ligands may be bridged one to another; the activator component comprises a cation, which may be a Bronsted acid capable of donating a proton (hereafter denoted as L'-H wherein L' is a neutral Lewis base and H is hydrogen), and a compatible noncoordinating anion. | | |

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ALUMINUM-FREE MONOCYCLOPENTADIENYL METALLOCENE
CATALYSTS FOR OLEFIN POLYMERIZATION

SPECIFICATION

FIELD OF THE INVENTION

This invention relates to certain transition metal compounds of the Group IV-B metals of the Periodic Table of Elements, to a catalyst system comprising such Group IV-B transition metal compounds and an ion-exchange activator compound, and to a process using such catalyst system for the production of polyolefins, particularly polyethylene, polypropylene, and ethylene- α -olefin copolymers.

BACKGROUND OF THE INVENTION

10 As is well known, various processes and catalysts exist for the homopolymerization or copolymerization of olefins. Traditional Ziegler-Natta catalyst systems--a transition metal compound

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cocatalyzed by an aluminum alkyl--are capable of producing polyolefins having a high molecular weight but a broad molecular weight distribution. Traditional types of Ziegler-Natta catalysts have very high activities, and the polyolefins produced therewith
5 have low catalyst residues and do not require a subsequent catalyst residue deashing treatment.

More recently a "metallocene" type catalyst system has been developed--one wherein the transition metal compound has cyclopentadienyl ring ligands, preferably at least two; such
10 transition metal compound being referred to as a "metallocene"--which catalyzes the production of olefin monomers to polyolefins. Accordingly, metallocene compounds of the Group IV-B metals, particularly bis(cyclopentadienyl) titanocenes and zirconocenes, have been utilized as the transition metal component in such "metallocene"
15 containing catalyst system for the production of polyolefins and ethylene- α -olefin copolymers. When such metallocenes are cocatalyzed with an aluminum alkyl--as is the case with a traditional type Ziegler-Natta catalyst system--the catalytic activity of such
20 metallocene catalyst system is generally too low to be of any commercial interest.

It has since become known that such metallocenes may be cocatalyzed with an alumoxane--rather than an aluminum alkyl--to
25 provide a metallocene catalyst system of high activity for catalyzing the production of moderately high molecular weight polyolefins. Unfortunately, the amount of alumoxane cocatalyst required to provide the metallocene component with high activity is generally high, generally expressed as a molar ratio of Al to transition metal, hence
30 a polyolefin produced from such metallocene-alumoxane catalyst may contain an undesirable amount of catalyst residue (or ash content, measured as the nonvolatile aluminum and transition metal content).

More recently, a new method of activating Group IV-B metallocene alkyl complexes was disclosed in European Patent
35 Applications Nos. 277,003 and 277,004. The improved metallocene catalysts are prepared by combining at least two components. The

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first component is a bis(cyclopentadienyl) derivative of a Group IV-B metal containing at least one ligand which will combine with the cationic portion of the second component. The second component is an ion-exchange reagent comprising a cation which will irreversibly
5 react with at least one ligand contained in said Group IV-B metal compound (first component) and a non-coordinating anion which is bulky, labile and stable. Suitable non-coordinating anions disclosed in these applications include: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated
10 to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of boron atoms such as carboranes, metallocarboranes and boranes. Upon combination of the first and second components, the cation of the second component reacts with one of the ligands of the first component, thereby
15 generating an ion-pair consisting of a Group IV-B metallocene cation with a formal coordination number of 3 and a valence of 4+ and the aforementioned non-coordinating anion. The disclosures are limited to catalyst systems derived from Group IV-B metallocene complexes containing at least two cyclopentadienyl ligands.

20 Aluminum alkyl-free olefin polymerization catalysts derived from transition metal complexes containing fewer than two cyclopentadiene have been relatively unexplored. John Bercaw reported [Organometallics, 1990, 9, 867] the synthesis of a monocyclopentadienyl scandium polymerization catalyst.
25 $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N-Bu}^t)\text{Sch}(\text{PMe}_3)]_2$ This neutral Group III catalyst has a low activity and is very expensive due to the high cost of scandium metal. The need exists to provide a method of preparing highly active, versatile, aluminum alkyl-free olefin polymerization catalysts derived from monocyclopentadienyl ligand
30 systems.

SUMMARY OF THE INVENTION

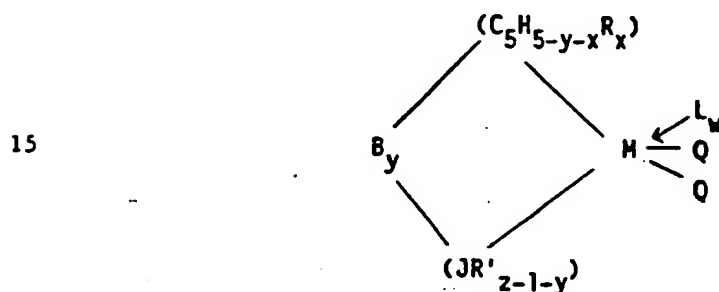
The catalyst system of this invention comprises a transition metal component from Group IV B of the Periodic Table of the Elements

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(CRC Handbook of Chemistry and Physics, 68th ed. 1987-1988) and an ion-exchange reagent which may be employed in solution, slurry, gas phase or bulk phase polymerization procedure to produce a polyolefin of high weight average molecular weight and relatively narrow molecular weight distribution.

5 In general the Group IV B transition metal component can be a polyalkyl or hydride complex containing fewer than two cyclopentadienyl groups.

The "Group IV B transition metal component" of the mono-cyclopentadienyl catalyst system is represented by the general
10 formula:



20 wherein: M is Zr, Hf or Ti and is in its highest formal oxidation state (+4, d^0 complex);

$(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring which is substituted with from zero to five substituent groups R, "x" is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each
25 substituent group R is, independently, a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals, substituted C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, C_1 - C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group
30 IV A of the Periodic Table of Elements, and halogen radicals; or
 $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming a C_4 - C_{20} ring to give a polycyclic cyclopentadienyl ligand such as indenyl and fluorenyl derivatives.

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(JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group V A or an element with a coordination number of two from Group VI A of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur, and each R' is, independently a radical selected from a group consisting of

5 C₁-C₂₀ hydrocarbyl radicals, substituted C₁-C₂₀ hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, and "z" is the coordination number of the element J;

each Q may be independently, hydride, C₁-C₅₀ hydrocarbyl radicals, substituted hydrocarbyl radicals wherein one or more

10 hydrogen atoms is replaced by an electron-withdrawing group such as a halogen atom, or alkoxide radical, or C₁-C₅₀ hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV-A of the Period Table of Elements, provided that were any Q is a hydrocarbyl such Q is different from

15 (C₅H_{5-y-x}R_x), or both Q together may be an alkylidene, olefin, acetylene or a cyclometallated hydrocarbyl.

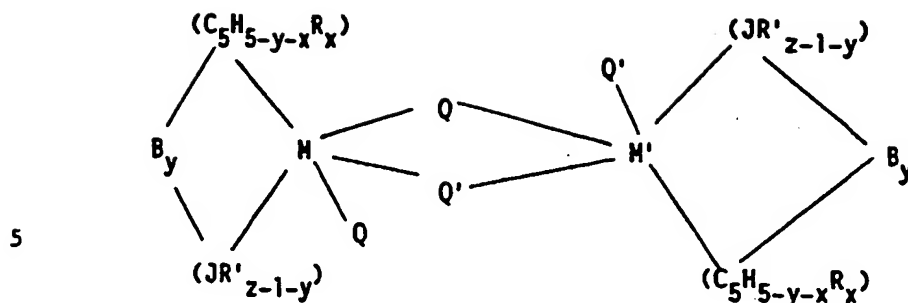
"y" is 0 or 1; when "y" is 1, B is a covalent bridging group containing a Group IV A or V A element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium radical, alkyl or

20 aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like;

L is a neutral Lewis base such as diethylether, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like; and "w" is a number from 0 to 3; L can

25 also be a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q', wherein M' has the same meaning as M and Q' has the same meaning as Q. Such compounds are represented by the formula:

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The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said Group IV-B metal compound and a noncoordinating anion which is bulky, labile, and stable. Upon combination of the first and second components, the cation of the second component reacts with one of the ligands of the first component, thereby generating an ion pair consisting of a Group IV-B metal cation with a formal coordination number of 3 and a valence of +4 and the aforementioned anion, which anion is compatible with and non-coordinating toward the metal cation formed from the first component. Illustrative but not limiting examples of cations of the second component include Bronstead acids such as ammonium ions or reducible Lewis acids such as Ag^+ or ferrocenium ions. The anion of the second compound must be capable of stabilizing the Group IV-B metal cation complex without interfering with the Group IV-B metal cation's or its decomposition product's ability to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization.

Catalyst systems of the invention may be prepared by placing the "Group IV B transition metal component" and the ion-exchange component in common solution in a normally liquid alkane or aromatic solvent, which solvent is preferably suitable for use as a polymerization diluent for the liquid phase polymerization of an olefin monomer. Suitable catalysts can also be prepared by

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reacting the components and adsorbing on a suitable support material (inorganic oxides or polymers, for example) or by allowing the components to react on such support.

5 A typical polymerization process of the invention such as for the polymerization or copolymerization of ethylene comprises the steps of contacting ethylene alone, or with other unsaturated monomers including C₃-C₂₀ α -olefins, C₅-C₂₀ diolefins, and/or acetylenically unsaturated monomers either alone or in combination with other olefins and/or other unsaturated monomers, 10 with a catalyst comprising, in a suitable polymerization diluent, the Group IV B transition metal component illustrated above; and the ion-exchange activator component in an amount to provide a molar transition metal to activator ratio of from about 1:10 to about 200:1 or more; and reacting such monomer in the presence of such catalyst 15 system at a temperature of from about -100°C to about 300°C for a time of from about 1 second to about 10 hours to produce a polyolefin having a weight average molecular weight of from about 1,000 or less to about 5,000,000 or more and a molecular weight distribution of about 1.5 or greater.

20 DESCRIPTION OF THE PREFERRED EMBODIMENT

Ionic Catalyst System - General Description

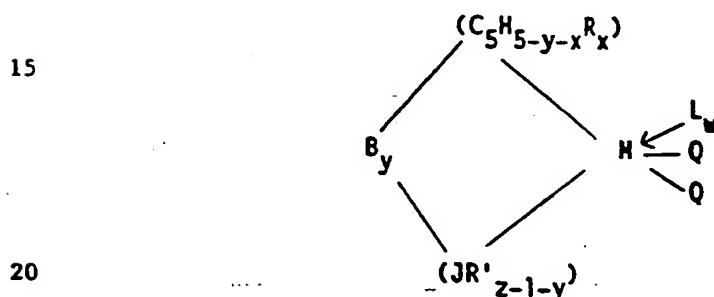
The process of this invention is practiced with that class of ionic catalysts prepared by combining at least two components. The first of these is a monocyclopentadienyl derivative of a Group 25 IV-B metal compound containing at least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained in said Group IV-B metal 30 compound and a noncoordinating anion which is bulky, labile, and stable. Upon combination of the first and second components, the cation of the second component reacts with one of the ligands of the first component, thereby generating an ion pair consisting of a

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Group IV-B metal cation with a formal coordination number of 3 and a valence of +4 and the aforementioned anion, which anion is compatible with and non-coordinating towards the metal cation formed from the first component. The anion of the second compound must be capable of stabilizing the Group IV-B metal cation complex without interfering with the Group IV-B metal cation's or its decomposition product's ability to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization.

10 A. Catalyst Component

The Group IV-B transition metal component of the catalyst system is represented by the general formula:



wherein: M is Zr, Hf or Ti and is in its highest formal oxidation state (+4, d^0 complex);

($\text{C}_5\text{H}_{5-y-x}\text{R}_x$) is a cyclopentadienyl ring which is substituted with from zero to five substituent groups R, "x" is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals, substituted C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, C_1 - C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements, and halogen radicals; or

$(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming a C_4-C_{20} ring to give a polycyclic cyclopentadienyl ligand such as indenyl and fluorenyl derivatives;

- 5 (JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group V A or an element with a coordination number of two from Group VI A of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur with nitrogen being preferred, and each R' is, independently a radical selected from a group consisting of
- 10 C_1-C_{20} hydrocarbyl radicals, substituted C_1-C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, and "z" is the coordination number of the element J;

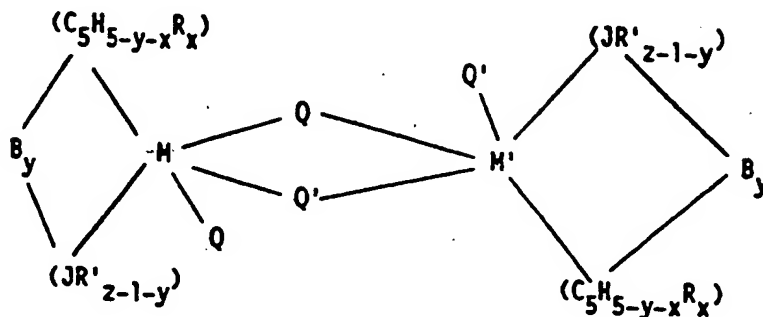
- each Q may be independently, hydride, C_1-C_{50} hydrocarbyl radicals, substituted hydrocarbyl radicals wherein one
- 15 or more hydrogen atoms is replaced by an electron-withdrawing group such as a halogen atom, or alkoxide radical, or C_1-C_{50} hydrocarbyl-substituted metalloids wherein the metalloid is selected from the Group IV-A of the Periodic Table of Elements, provided that where any Q is a hydrocarbyl such Q is different from
- 20 $(C_5H_{5-y-x}R_x)$, or both Q together may be an alkylidene olefin, acetylene or a cyclometallated hydrocarbyl;

- "y" is 0 or 1; when "y" is 1, B is a covalent bridging group containing a Group IV A or V A element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium
- 25 radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like. Examples of the B group which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in Column 1 of Table 1 under the heading "B".

- 30 L is a neutral Lewis base such as diethylether, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like; and "w" is a number from 0 to 3; L can also be a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q'.

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wherein M' has the same meaning as M and Q' has the same meaning as Q. Such compounds are represented by the formula:



- 5 Exemplary hydrocarbyl radicals for the Q are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like, with methyl being preferred. Exemplary substituted hydrocarbyl radicals include trifluoromethyl, pentafluorophenyl, trimethylsilylmethyl, and trimethoxysilylmethyl and the like. Exemplary hydrocarbyl substituted metalloids include trimethylsilyl, trimethylgermyl, triphenylsilyl, and the like. Exemplary alkyldiene radicals for both Q together are methylidene, ethylidene and propylidene. Examples of the Q group which are suitable as a constituent group or element of the Group IV B transition metal component of the catalyst system are identified in Column 4 of Table 1 under the heading "Q".

- 20 Suitable hydrocarbyl and substituted hydrocarbyl radicals, which may be substituted as an R group for at least one hydrogen atom in the cyclopentadienyl ring, will contain from 1 to about 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals. Suitable organometallic radicals, which may be substituted as an R group for at least one hydrogen atom in the

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cyclopentadienyl ring, include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, trimethylgermyl and the like. Examples of cyclopentadienyl ring groups ($C_5H_{5-y-x}R_x$) which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in Column 2 of Table 1 under the heading ($C_5H_{5-y-x}R_x$).

Suitable hydrocarbyl and substituted hydrocarbyl radicals, which may be substituted as an R' group for at least one hydrogen atom in the heteroatom J ligand group, will contain from 1 to about 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals. Examples of heteroatom ligand groups (JR'_{z-1-y}) which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in Column 3 of Table 1 under the heading (JR'_{z-1-y}).

Table 1 depicts representative constituent moieties for the "Group IV B transition metal component", the list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting all possible combinations of the constituent moieties with each other. Illustrative compounds are: dimethylsilyltetramethylcyclopentadienyl-tert-butylamido zirconium dimethyl, dimethylsilyltetramethylcyclopentadienyl-tert-butylamido hafnium diethyl, dimethylsilyl-tert-butylcyclopentadienyl-tert-butyl- amido zirconium dihydride, dimethylsilyl-tert-butylcyclopentadienyl-tert-butylamido hafnium diphenyl, dimethylsilyltrimethylsilylcyclopentadienyl-tert-butylamido zirconium dihydride, dimethylsilyltetramethylcyclopentadienylphenylamido titanium dimethyl, dimethylsilyltetramethylcyclopentadienylphenylamido hafnium ditolyl, methylphenylsilyltetramethylcyclopentadienyl-tert-butylamido zirconium dihydride, methylphenylsilyltetramethylcyclopentadienyl-tert-butylamido hafnium dimethyl,

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dimethylsilylfluorenyl-cyclohexylamide titanium dimethyl,
 diphenylgermylindenyl-t-butyl phosphido dihydride,
 methylphenylsilyltetramethylcyclopentadienyl-~~tert~~-butylamido
 hafnium dimethyl, dimethylsilyltetramethylcyclopentadienyl-p-n-
 5 butylphenylamido zirconium dihydride, dimethylsilyltetramethyl-
 cyclopentadienyl-p-n-butylphenylamido hafnium ditrimethylsilyl.
 For illustrative purposes, the above compounds and those permuted
 from Table 1 do not include the neutral Lewis base ligand (L). The
 conditions under which complexes containing neutral Lewis base
 10 ligands such as ether or those which form dimers is determined by
 the steric bulk of the ligands about the metal center. Similarly,
 due to the decreased steric bulk of the
 trimethylsilylcyclopentadienyl group in
 $[\text{Me}_2\text{Si}(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{N-t-Bu})\text{ZrH}_2]_2$ versus that of the
 15 tetramethylcyclopentadienyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{-ZrH}_2$,
 the former compound is dimeric and the latter is not.

Generally the bridged species of the Group IV B transition
 metal compound ("y"-1) are preferred. A preferred method of
 preparing these compounds is by reacting a cyclopentadienyl lithium
 20 compound with a

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dihalo-compound whereupon a lithium halide salt is liberated and a monohalo substituent becomes covalently bound to the cyclopentadienyl compound. The so substituted cyclopentadienyl reaction product is next reacted with a lithium salt of a phosphide, oxide, sulfide or amide (for the sake of illustration, a lithium amide) whereupon the halo element of the monohalo substituent group of the reaction product reacts to liberate a lithium halide salt and the amine moiety of the lithium amide salt becomes covalently bound to the substituent of the cyclopentadienyl reaction product. The resulting amine derivative of the cyclopentadienyl product is then reacted with an alkyl lithium reagent whereupon the labile hydrogen atoms, at the carbon atom of the cyclopentadienyl compound and at the nitrogen atom of the amine moiety covalently bound to the substituent group, react with the alkyl of the lithium alkyl reagent to liberate the alkane and produce a dilithium salt of the cyclopentadienyl compound. Thereafter the bridged species of the Group IV B transition metal compound is produced by reacting the dilithium salt cyclopentadienyl compound with a Group IV B transition metal preferably a Group IV B transition metal halide. This procedure yields the dichloro-derivative of the monocyclopentadienyl-amido Group IV-B compound. The dichloride complex is then converted into the appropriate hydrocarbyl derivative using the corresponding Grignard, lithium, sodium or potassium salt of the hydrocarbyl ligand. The procedures used are analogous to those developed for alkylating the Group IV-B metallocene complexes (i.e., the bis-cyclopentadienyl) systems).

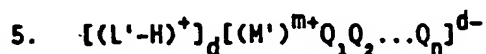
Unbridged species of the Group IV B transition metal compound can be prepared from the reaction of a cyclopentadienyl lithium compound and a lithium salt of an amine with a Group IV B transition metal halide.

Suitable, but not limiting, Group IV B transition metal compounds which may be utilized in the catalyst system of this invention include those bridged species ("y"-1) wherein the B group

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lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of boron atoms such as carboranes, metallocarboranes and boranes.

In general, activator compounds containing single
 5 anionic coordination complexes which are useful in this invention may be represented by the following general formula:



10 Wherein:

L' is a neutral Lewis base;

H is a hydrogen atom;

[L'-H] is a Bronsted acid;

M' is a metal or metalloid selected from the Groups
 15 subtended by Groups V-B to V-A of the Periodic Table of the Elements; i.e., Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A;

Q₁ to Q_n are selected, independently, from the Group consisting of hydride radicals, dialkylamido radicals,
 20 alkoxide and aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals and organometalloid radicals and any one, but not more than one, of Q₁ to Q_n may be a halide radical, the remaining Q₁ to Q_n being, independently, selected from the foregoing radicals;

25 m is an integer from 1 to 7;

n is an integer from 2 to 8; and n - m = d.

As indicated above, any metal or metalloid capable of forming an anionic complex which is stable in water may be used or contained in the anion of the second compound. Suitable metals,
 30 then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes containing a single

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metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

The preferred activator compounds comprising boron may be represented by the following general formula:



Wherein:

L' is a neutral Lewis base;

H is a hydrogen atom;

[L'-H]⁺ is a Bronsted acid;

B is boron in a valence state of 3;

Ar₁ and Ar₂ are the same or different aromatic or substituted-aromatic hydrocarbon radicals containing from about 6 to about 20 carbon atoms and may be linked to each other through a stable bridging group; and

X₃ and X₄ are radicals selected,

independently, from the group consisting of hydride radicals, halide radicals, with the proviso that X₃ and X₄ will not be halide at the same time, hydrocarbyl radicals containing from 1 to about 20 carbon atoms, substituted-hydrocarbyl radicals, wherein one or more of the hydrogen atoms is replaced by a halogen atom, containing from 1 to about 20 carbon atoms, hydrocarbyl-substituted metal (organometalloid) radicals wherein each hydrocarbyl substitution contains from 1 to about 20 carbon atoms and said metal is selected from Group IV-A of the Periodic Table of the Elements and the like.

In general, Ar₁ and Ar₂ may, independently, be any aromatic or substituted-aromatic hydrocarbon radical containing from about 6 to about 20 carbon atoms. Suitable aromatic radicals include, but are not limited to, phenyl, naphthyl and anthracenyl

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radicals. Suitable substituents on the substituted-aromatic hydrocarbon radicals, include, but are not necessarily limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy radicals, alkylamido radicals, fluoro and fluorohydrocarbyl radicals and the like such as those useful as X_3 and X_4 . The substituent may be ortho, meta or para, relative to the carbon atoms bonded to the boron atom. When either or both X_3 and X_4 are a hydrocarbyl radical, each may be the same or a different aromatic or substituted-aromatic radical as are Ar_1 and Ar_2 , or the same may be a straight or branched alkyl, alkenyl or alkynyl radical having from 1 to about 20 carbon atoms, a cyclic hydrocarbon radical having from about 5 to about 8 carbon atoms or an alkyl-substituted cyclic hydrocarbon radical having from about 6 to about 20 carbon atoms. X_3 and X_4 may also, independently, be alkoxy or dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals contain from 1 to about 20 carbon atoms, hydrocarbyl radicals and organometalloid radicals having from 1 to about 20 carbon atoms and the like. As indicated above, Ar_1 and Ar_2 may be linked to each other. Similarly, either or both of Ar_1 and Ar_2 could be linked to either X_3 or X_4 . Finally, X_3 or X_4 may also be linked to each other through a suitable bridging group.

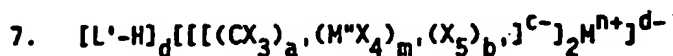
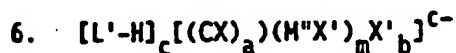
Illustrative, but not limiting, examples of boron compounds which may be used as an activator component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as triethylammonium tetra(phenyl)boron, tripropylammonium tetra(phenyl)boron, tri(n-butyl)ammonium tetra(phenyl)boron, trimethylammonium tetra(p-tolyl)boron, trimethylammonium tetra(o-tolyl)boron, tributylammonium tetra(pentafluorophenyl)boron, tripropylammonium tetra(o,p-dimethylphenyl)boron, tributylammonium tetra(m,m-dimethylphenyl)boron, tributylammonium tetra(p-tri-fluoromethylphenyl)boron, tri(n-butyl)ammonium tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium salts such

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as N,N-dimethylanilinium tetra(pentafluoro phenyl)boron,
 N,N-diethylanilinium tetra(phenyl)boron,
 N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron and the like;
 dialkyl ammonium salts such as di(1-propyl)ammonium
 5 tetra(pentafluorophenyl)boron, dicyclohexylammonium
 tetra(phenyl)boron and the like; and triaryl phosphonium salts such
 as triphenylphosphonium tetra(phenyl)boron,
 tri(methylphenyl)phosphonium tetra(phenyl)boron,
 tri(dimethylphenyl)phosphonium tetra(phenyl)boron and the like.

10 Similar lists of suitable compounds containing other
 metals and metalloids which are useful as activator components may
 be made, but such lists are not deemed necessary to a complete
 disclosure. In this regard, it should be noted that the foregoing
 list is not intended to be exhaustive and that other useful boron
 15 compounds as well as useful compounds containing other metals or
 metalloids would be readily apparent to those skilled in the art
 from the foregoing general equations.

Activator components based on anions which contain a
 plurality of boron atoms may be represented by the following
 20 general formulae:



25 wherein $[L'-H]$ is a cation, e.g., H^+ , ammonium or a substituted
 ammonium cation having up to 3 hydrogen atoms replaced with a
 hydrocarbyl radical containing from 1 to about 20 carbon atoms or a
 substituted-hydrocarbyl radical, wherein one or more of the hydrogen
 atoms is replaced by a halogen atom, containing from 1 to about 20
 30 carbon atoms, phosphonium radicals, substituted-phosphonium
 radicals having up to 3 hydrogen atoms replaced with a hydrocarbyl
 radical containing from 1 to about 20 carbon atoms or a
 substituted-hydrocarbyl radical, wherein 1 or more of the hydrogen

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atoms is replaced by a halogen atom, containing from 1 to about 20 carbon atoms and the like; C is carbon; Mⁿ is boron or phosphorus; each of X, X', X'', X₃, X₄, and X₅ are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals containing from 1 to about 20 carbon atoms, substituted-hydrocarbyl radicals, wherein one or more of the hydrogen atoms is replaced by a halogen atom, containing from 1 to 20 carbon atoms, organometalloid radicals wherein each hydrocarbyl substitution in the organo portion contains from 1 to about 20 carbon atoms and said metal is selected from Group IV-A of the Periodic Table of the Elements and the like; M is a transition metal; "a" and "b" are integers > 0; "c" is an integer > 1; a + b + c = an even-numbered integer from 2 to about 8; and "m" is an integer ranging from 5 to about 22; "a'" and "b'" are the same or a different integer > 0; "c'" is an integer > 2; a' + b' + c' = an even-numbered integer from 4 to about 8; "m'" is an integer from 6 to about 12; "n" is an integer such that 2c' - n = d; and "d" is an integer greater than or equal to 1.

Illustrative, but not limiting, examples of second components which can be used in preparing catalyst systems utilized in the process of this invention wherein the anion of the second component contains a plurality of metalloid atoms (as in formulae 5 and 6) are ammonium salts such as ammonium 1-carbadodecaborate (using 1-carbadodecaborate as an illustrative, but not limiting, counterion for the ammonium cations listed below): monohydrocarbyl-substituted ammonium salts such as methylammonium 1-carbadodecaborate, ethylammonium 1-carbadodecaborate, propylammonium 1-carbadodecaborate, isopropylammonium 1-carbadodecaborate, (n-butyl)ammonium 1-carbadodecaborate, anilinium 1-carbadodecaborate, and (p-tolyl)ammonium 1-carbadodecaborate and the like; dihydrocarbyl-substituted ammonium salts such as dimethylammonium 1-carbadodecaborate, diethylammonium 1-carbadodecaborate, dipropylammonium 1-carbadodecaborate, diisopropylammonium 1-carbadodecaborate, di(n-butyl) ammonium

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- 1-carbadodecaborate, diphenylammonium 1-carbadodecaborate,
di(p-tolyl)ammonium 1-carbadodecaborate and the like;
trihydrocarbyl-substituted ammonium salts such as trimethylammonium
1-carbadodecaborate, triethylammonium 1-carbadodecaborate,
5 tripropyl-ammonium 1-carbadodecaborate, tri(n-butyl) ammonium
1-carbadodecaborate, triphenylammonium 1-carbadodecaborate,
tri(p-tolyl)ammonium 1-carbadodecaborate, N,N-dimethylanilinium
1-carbadodecaborate, N,N-diethylanilinium 1-carbadodecaborate and
the like.
- 10 Illustrative, but not limiting examples of second compounds
corresponding to Formula 5 [using tri(n-butyl)ammonium as an
illustrative, but not limiting, counterion for the anions listed
below] are salts of anions such as bis[tri(n-butyl)ammonium]
nonaborate, bis[tri(n-butyl)ammonium]decaborate, bis[tri(n-butyl)
15 ammonium]undecaborate, bis[tri(n-butyl)ammonium] dodecaborate,
bis[tri(n-butyl)ammonium]decachlorodecaborate, tri(n-butyl)ammonium
dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate,
tri(n-butyl) ammonium 1-carbaundecaborate, tri(n-butyl)ammonium
1-carbadodecaborate, tri(n-butyl)ammonium
20 1-trimethylsilyl-1-carbadecaborate, tri(n-butyl)ammonium
dibromo-1-carbadodecaborate and the like; borane and carborane
complexes and salts of borane and carborane anions such as
decaborane(14), 7,8-dicarbaundecaborane(13),
2,7-dicarbaundecaborane(13),
25 undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane,
dodecahydrido-11-methyl-2,7-di-carbaundecaborane, tri(n-butyl)
ammonium undecaborate(14), tri(n-butyl)ammonium
6-carbadecaborate(12), tri(n-butyl)ammonium 7-carbaundecaborate(13),
tri(n-butyl)ammonium 7,8-dicarbaundecaborate(12),
30 tri(n-butyl)ammonium 2,9-dicarbaundecaborate(12),
tri(n-butyl)ammonium dodecahydrido-8-methyl-7,9-dicarbaundecaborate,
tri(n-butyl)ammonium undecahydrido-8-ethyl-7,9-dicarbaundecaborate,
tri(n-butyl) ammonium undecahydrido-8-butyl-7,9-dicarbaundecaborate,
tri(n-butyl)ammonium undecahydrido-8-allyl-7,9-dicarbaundecaborate,

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tri(n-butyl)ammonium
 undecahydrido-9-trimethylsilyl-7,8-dicarbaundecaborate,
 tri(n-butyl)ammonium undecahydrido-4,6-dibromo-7-carbaundecaborate
 and the like; boranes and carboranes and salts of boranes and
 5 carboranes such as 4-carbanonaborane(14), 1,3-dicarbanonaborane(13),
 6,9-dicarbadeccaborane(14),
 dodecahydrido-1-phenyl-1,3-dicarbanonaborane,
 dodecahydrido-1-methyl-1,3-dicarbanonaborane,
 undecahydrido-1,3-dimethyl-1,3-dicarbanonaborane and the like.

10 Illustrative, but not limiting, examples of second
 compounds corresponding to Formula 7 [using tri(n-butyl)ammonium as
 an illustrative, but not limiting, counterion for the anions listed
 below] are salts of metallocarborane and metallocaborane anions such
 as tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbaunaborato)

15 cobaltate(III), tri(n-butyl)ammonium
 bis(undeca-hydrido-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)
 ammonium bis(undecahydrido-7,8-dicarbaundecaborato)cobaltate(III),
 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaunaborato)
 nikelate(III), tri(n-butyl)ammonium bis(nonahydrido-7,

20 8-dimethyl-7,8-dicarbaundecaborato)ferrate(III),
 tri(n-butyl)ammonium
 bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundecaborato)chromate(III),
 tri(n-butyl)ammonium
 bis(tribromooctahydrido-7,8-dicarbaundecaborato)cobaltate(III),

25 tri(n-butyl)ammonium bis(dodecahydridodicarbadeccaborato)
 cobaltate(III), tris[tri(n-butyl)ammonium] bis
 (undecahydrido-7-carbaundecaborato)chromate(III), bis[tri(n-butyl)
 ammonium] bis(undecahydrido-7-carbaundecaborato)manganate(IV),
 bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborato)

30 cobaltate(III), bis[tri(n-butyl)ammonium]
 bis(undecahydrido-7-carbaundecaborato)nickelate(IV) and the like.
 A similar list of representative phosphonium compounds can be
 recited as illustrative second compounds, but for the sake of
 brevity, it is simply noted that the phosphonium and

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substituted-phosphonium salts corresponding to the listed ammonium and substituted-ammonium salts could be used as second compounds in the present invention.

Process of Catalyst Preparation

5 The catalyst systems employed in the method of the invention comprise a complex formed upon admixture of the Group IV-B transition metal component with the activator component. The catalyst system may be prepared by addition of the requisite Group IV-B transition metal and activator components to an inert solvent
10 in which olefin polymerization can be carried out by a solution polymerization procedure.

 The catalyst system may be conveniently prepared by placing the selected Group IV-B transition metal component and the selected activator component, in any order of addition, in an alkane or
15 aromatic hydrocarbon solvent -- preferably toluene. The catalyst system may be separately prepared, in concentrated form, and added to the polymerization diluent in a reactor. Or, if desired, the components of the catalyst system may be prepared as separate solutions and added to the polymerization diluent in a reactor, in
20 appropriate ratios, as is suitable for a continuous liquid polymerization reaction procedure. Alkane and aromatic hydrocarbons suitable as solvents for formation of the catalyst system and also as a polymerization diluent are exemplified by, but are not necessarily limited to, straight and branched chain hydrocarbons
25 such as isobutene, butane, pentane, hexane, heptane, octane and the like, cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane and the like, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and the like. Suitable solvents also
30 include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butene, 1-hexene and the like.

 In accordance with this invention optimum results are generally obtained wherein the Group IV-B transition metal compound

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is present in the polymerization diluent in concentration of from about 0.01 to about 1.0 millimoles/liter of diluent and the activator component is present in an amount to provide a molar ratio of the transition metal to activator component from about 1:1 to about 200:1. Sufficient solvent should be employed so as to provide adequate heat transfer away from the catalyst components during reaction and to permit good mixing.

The catalyst system ingredients -- that is, the Group IV-B transition metal and activator components, and polymerization diluent can be added to the reaction vessel rapidly or slowly. The temperature maintained during the contact of the catalyst components can vary widely, such as, for example, from -10° to 300°C . Greater or lesser temperatures can also be employed. Preferably, during formation of the catalyst system, the reaction is maintained within a temperature of from about 25° to 100°C , most preferably about 25°C .

At all times, the individual catalyst system components, as well as the catalyst system once formed, are protected from oxygen and moisture. Therefore, the reactions are performed in an oxygen and moisture free atmosphere and, where the catalyst system is recovered separately, it is recovered in an oxygen and moisture free atmosphere. Preferably, therefore, the reactions are performed in the presence of an inert dry gas such as, for example, helium or nitrogen.

The Catalyst System: Characterization and Properties of the Active Site

The reaction of the two catalyst components can be viewed as a simple acid-base reaction where the Q^{-} -ligand bound to the transition metal center of $(\text{CN})\text{MQ}_2$ (where $(\text{CN}) = \text{Cp}$ and J -ligands) reacts with the cation of the second component, which may be acidic, $[\text{L}'\text{H}^{+}][\text{A}^{-}]$ (where A^{-} is the non-coordinating anion), to give the ionic catalyst $[(\text{CN})\text{MQ}^{+}][\text{A}^{-}]$ and neutral biproducts Q-H and L' . The overall catalytic performance of the catalyst depends on the choice of metal, the specific (CN) -ligand set, the structure and

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stability of A^- , and the coordinating ability of the cation or Lewis base L' . For conventional applications where a high productivity homopolymerization or random copolymerization catalyst is desired, the cation is a proton donor and the Q-ligand of the transition metal component is chosen so that: 1) 5 the metal complex is easy to prepare and is low cost, 2) $(CN)MQ_2$ is sufficiently basic to deprotonate the acidic cation of the activator component, and 3) Q-H is an unreactive biproduct such as an alkane so that the activation reaction is irreversible. For a particular $(CN)M$ -system the L' and A^- portions of the activator 10 component "tune" the stability and overall performance of the catalyst system. The ability of L' and A^- to modify the behavior of a catalyst site increases the versatility of the polymerization system which is an important advantage over conventional methods of activation (e.g. methylalumoxane, and other aluminum alkyl 15 cocatalysts).

In general, and while most transition metal components identified above may be combined with most activator components identified above to produce an active olefin polymerization catalyst, it is important for continuity of the polymerization 20 operations that either the metal cation initially formed from the first component or a decomposition product thereof be a relatively stable catalyst. It is also important that the anion of the activator compound be stable to hydrolysis when an ammonium salt is used. Further, it is important that the positive charge 25 of the activator component be sufficient, relative to the metal component, to facilitate the needed cation, e.g., proton transfer. Activator compounds containing aryl-ammonium salts such as N,N-dimethylanilium are more acidic than trialkylammonium salts and therefore are useful with a wider variety of transition metal components. The basicity of the 30 metal complex must also be sufficient to facilitate the needed proton transfer. In general, transition metal compounds which can be hydrolyzed by aqueous solutions can be considered suitable as metallocene components to form the catalysts described herein.

With respect to the combination of the transition metal

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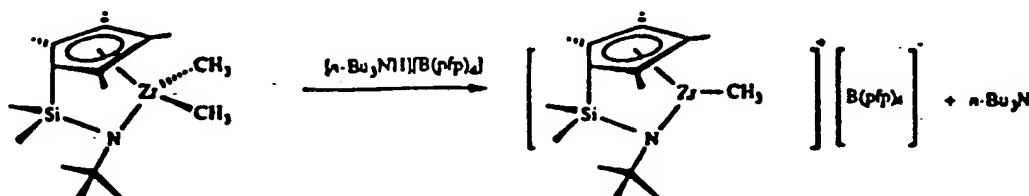
component with the activator component to form a catalyst of this invention, it should be noted that the two compounds combined for preparation of the active catalyst must be selected so as to avoid transfer of a fragment of the anion to the metal cation, thereby forming a catalytically inactive species. This could be done by steric hindrance, resulting from substitutions on the Cp- and/or J-ligands of the first component, as well as substitutions on the non-coordinating anion.

As the amount and size of the substitutions on the transition metal components are reduced, more effective catalysts are obtained with activator compounds containing non-coordinating anions which are larger in size and more resistant to degradation. In the case where the non-coordinating anion is an anionic coordination complex, such as a tetraphenylboron derivative, substitutions on the phenyl rings can be used to prevent the transfer of a proton or an entire phenyl group from the anion to the metal. This can be accomplished by alkyl substitution in the ortho positions of the phenyl groups, or, more preferably, by perfluoro-substitutions on the anion. Thus, anionic coordination complexes containing perfluorophenyl-, trifluoromethylphenyl-, or bis-trifluoromethylphenyl rings are preferred for this subgenus of activator components. When the non-coordinating anion contains a plurality of boron atoms as described in general formulae 6 and 7, more effective catalysts are obtained with activator compounds containing larger anions, such as those encompassed by Equation 7 and those having larger m values in Equation 6. In these cases it is further preferable when using second compounds which are encompassed by Equation 6, that $a + b + c = 2$. Second compounds in which $a + b + c =$ even-numbered integers of 4 or more have acidic B-H-B moieties which can react further with the metal cation formed, leading to catalytically inactive compounds.

Several new compositions of matter have been identified using high field NMR spectroscopy. The reaction between $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrMe}_2$ and $[\text{DMAH}][\text{B}(\text{pfp})_4]$ (where DMAH

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- PhMe_2NH^+ and $\text{pfp} = \text{C}_6\text{F}_5$) in d^8 -toluene produces a two phase system. The top layer is largely d^8 -toluene with only a very small amount of DMA (DMA = PhNMe_2) present. The lower layer contains the ionic catalyst and d^8 -toluene. The high field ^{13}C NMR spectrum of the lower layer suggests the reaction proceeds to give the DMA-adduct as shown below.

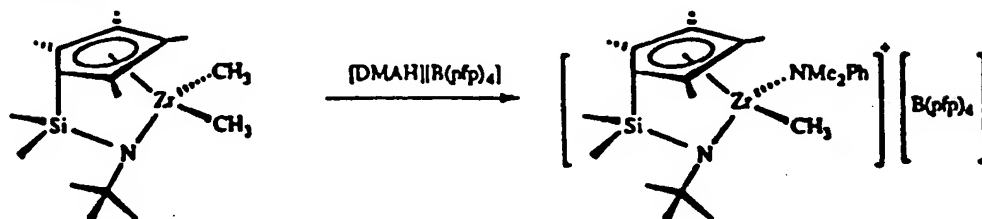


The NMR data clearly suggest that the amine is indeed coordinated to the zirconium atom, but that it is fluxional and probably has two orientations of coordination, most likely in the form of rotational isomers. The ionic catalysts species can be crystallized out at -40°C giving a pale powder. The solid state NMR spectrum of this material revealed amine coordination to the zirconium atom with more than one orientation. Addition of d^8 -thf (thf = tetrahydrofuran) to the catalyst solution or solid produces the d^8 -thf adduct, $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrMe}(\text{d}^8\text{-thf})_x][\text{B}(\text{pfp})_4]$ and free DMA. This was expected since d^8 -thf is a much stronger base than DMA.

Ion-exchange activators with different basicities have also been investigated. An amine which is a stronger base than DMA, such as DMT ($\text{Me}_2\text{N-p-Me-Ph}$) provides complete coordination to the zirconium atom with no fluxionality. This catalyst was produced from the reaction of $[\text{DMTH}][\text{B}(\text{pfp})_4]$ with $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrMe}_2$. Very little, if any, free DMT was observed in the ^{13}C NMR spectrum of the catalyst solution. The use of $[\text{Bu}_3\text{NH}][\text{B}(\text{pfp})_4]$ as the activator provided a more

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interesting result. It appears that when $[n\text{-Bu}_3\text{NH}][\text{B}(\text{pfp})_4]$ is reacted with $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrMe}_2$, the amine does not coordinate to the zirconium atom as illustrated in the equation below.



- 5 The fact that the amine is not coordinated to the metal is evidenced by the fact that the chemical shift of the amine signals are unchanged from free-amine. From a purely electronic point of view one would predict that Bu_3N would be a better ligand for the cationic metal center than DMA. The reverse is the case in this system indicating that steric forces dominate the coordination chemistry. The observation of two Cp-methyl signals and one Me_2Si -signal suggests that the cation is a symmetric three coordinate cation and that anion and the amine ligand to not coordinate strongly with the metal to destroy the plane of symmetry through the metal, the Cp-centroid, and the silicon atom.

10 The reaction of $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrMe}_2$ with $[\text{DMAH}][(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}]$ was also investigated by high field NMR. In this case the amine, DMA, is not coordinated to the metal. The fact that one observes four Cp-methyl signals and two Me_2Si signals in the ^{13}C NMR spectrum suggests that the metallacarborane is coordinated to the metal center. This is consistent with its high solubility and low activity relative to the $\text{B}(\text{pfp})_4^-$ system.

Polymerization Process

- 25 In a preferred embodiment of the process of this invention the catalyst system is utilized in a liquid phase polymerization of an olefin monomer. The liquid phase process comprises the steps of contacting an olefin monomer with the catalyst system in a suitable

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polymerization diluent and reacting said monomer in the presence of said catalyst system for a time and at a temperature sufficient to produce a polyolefin.

5 The monomer for such process may comprise ethylene alone, for the production of a homopolyethylene, or ethylene in combination with an α -olefin having 3 to 18 carbon atoms for the production of an ethylene- α -olefin copolymer. Conditions most preferred for the homo- or copolymerization of ethylene are those wherein ethylene is submitted to the reaction zone at pressures of from about 0.019 psi
10 to about 50,000 psi and the reaction temperature is maintained at from about -100°C to about 300°C, preferably -10° to 220°C. The mole ratio of transition metal component to activator component is preferably from about 1:1 to about 200:1. The reaction time is preferably from about 1 second to about 1 hour.

15 Without limiting in any way the scope of the invention, one means for carrying out the process of the present invention is as follows: in a stirred-tank reactor liquid 1-butene monomer is introduced. The catalyst system is introduced via nozzles in either the vapor or liquid phase. Feed ethylene gas is introduced either
20 into the vapor phase of the reactor, or sparged into the liquid phase as is well known in the art. The reactor contains a liquid phase composed substantially of liquid 1-butene together with dissolved ethylene gas, and a vapor phase containing vapors of all monomers. The reactor temperature and pressure may be controlled
25 via reflux of vaporizing α -olefin monomer (autorefrigeration), as well as by cooling coils, jackets, etc. The polymerization rate is controlled by the rate of catalyst addition, or by the concentration of catalyst. The ethylene content of the polymer product is determined by the ratio of ethylene to 1-butene in the reactor,
30 which is controlled by manipulating the relative feed rates of these components to the reactor.

Examples

In the examples which illustrate the practice of the

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invention the analytical techniques described below were employed for the analysis of the resulting polyolefin products. Molecular weight determinations for polyolefin products were made by Gel Permeation Chromatography (GPC) according to the following technique. Molecular weights and molecular weight distributions were measured using a Waters 150 gel permeation chromatograph equipped with a differential refractive index (DRI) detector and a Chromatix KMX-6 on-line light scattering photometer. The system was used at 135°C with 1,2,4-trichlorobenzene as the mobile phase. Shodex (Showa Denko America, Inc.) polystyrene gel columns 802, 803, 804 and 805 were used. This technique is discussed in "Liquid Chromatography of Polymers and Related Materials III", J. Cazes, Editor, Marcel Dekker, 1981, p. 207 which is incorporated herein by reference. No corrections for column spreading were employed; however, data on generally accepted standards, e.g. National Bureau of Standards Polyethylene 1484 and anionically produced hydrogenated polyisoprenes (an alternating ethylene-propylene copolymer) demonstrated that such corrections on Mw/Mn (=MWD) were less than 0.05 units. Mw/Mn was calculated from elution time. The numerical analyses were performed using the commercially available Beckman/CIS customized LALLS software in conjunction with the standard Gel Permeation package, run on a HP 1000 computer.

The following examples are intended to illustrate specific embodiments of the invention and are not intended to limit the scope of the invention.

All procedures were performed under an inert atmosphere of helium or nitrogen. Solvent choices are often optional, for example, in most cases either pentane or 30-60 petroleum ether can be interchanged. The choice between tetrahydrofuran (thf) and diethyl ether is more restricted, but in several reactions, either could be used. The lithiated amides were prepared from the corresponding amines and either *n*-BuLi or MeLi. Published methods for preparing LiHC_5Me_4 include C.M. Fendrick et al. Organometallics, 3,819 (1984) and F.H. Kohler and K.H. Doll, Z. Naturforsch., 37b, 144 (1982). Other lithiated substituted

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cyclopentadienyl compounds are typically prepared from the corresponding cyclopentadienyl ligand and BuLi or MeLi, or by reaction of MeLi with the proper solvent. $ZrCl_4$ and $HfCl_4$ were purchased from either Aldrich Chemical Company or Cerac. Amines, silane and lithium reagents were purchased from Aldrich Chemical Company or Petrarch Systems. Activator components were prepared by known literature methods.

EXAMPLES

Synthesis of Mono-Cyclopentadienyl Complexes

1. $Me_2Si(C_5Me_4)(N-t-Bu)ZrMe_2$

Part 1. Me_4HC_5Li (10.0 g, 0.078 mol) was slowly added to a Me_2SiCl_2 (11.5 ml, 0.095 mol, in 225 ml of tetrahydrofuran (thf) solution). The solution was stirred for 1 hour to assure complete reaction. The thf solvent was then removed via a vacuum to a cold trap held at $-196^\circ C$. Pentane was added to precipitate out the LiCl. The mixture was filtered through Celite. The solvent was removed from the filtrate. $Me_4HC_5SiMe_2Cl$ (15.34 g, 0.071 mol) was recovered as a pale yellow liquid.

Part 2. $Me_4HC_5SiMe_2Cl$ (10.0 g, 0.047 mol) was slowly added to a suspension of $LiHN-t-Bu$ (3.68 g, 0.047 mol, ~ 100 ml thf). The mixture was stirred overnight. The thf was then removed via a vacuum to a cold trap held at $-196^\circ C$. Petroleum ether (~ 100 ml) was added to precipitate out the LiCl. The mixture was filtered through Celite. The solvent was removed from the filtrate. $Me_2Si(Me_4HC_5)(HN-t-Bu)$ (11.14 g, 0.044 mol) was isolated as a pale yellow liquid.

Part 3. $Me_2Si(Me_4HC_5)(HN-t-Bu)$ (11.14 g, 0.044 mol) was diluted with ~ 100 ml Et_2O . MeLi (1.4 M, 64 ml, 0.090 mol) was slowly added. The mixture was allowed to stir for 1/2 hour after the final addition of MeLi. The ether was reduced in volume prior to filtering off the product. The product, $[Me_2Si(Me_4C_5)(N-t-Bu)]Li_2$, was washed with several small portions of ether, then vacuum dried.

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- Part 4. $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}-t\text{-Bu})]\text{Li}_2$ (3.0 g, 0.011 mol) was suspended in ~150 ml Et_2O . ZrCl_4 (2.65 g, 0.011 mol) was slowly added and the resulting mixture was allowed to stir overnight. The ether was removed via a vacuum to a cold trap held at -196°C . Pentane was added to precipitate out the LiCl . The mixture was filtered through Celite twice. The pentane was significantly reduced in volume and the pale yellow solid was filtered off and washed with solvent.
- 5 $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}-t\text{-Bu})\text{ZrCl}_2$ (1.07 g, 0.0026 mole) was recovered. Additional $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}-t\text{-Bu})\text{ZrCl}_2$ was recovered from the filtrate by repeating the recrystallization procedure. Total yield, 1.94 g, 0.0047 mol).

- Part 5. $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}-t\text{-Bu})\text{ZrMe}_2$ was prepared by adding a stoichiometric amount of MeLi (1.4 M in ether) to
- 15 $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}-t\text{-Bu})\text{ZrCl}_2$ suspended in ether. The white solid was isolated in an 83% yield.

2. $\text{MePhSi}(\text{C}_5\text{Me}_4)(\text{N}-t\text{-Bu})\text{HfMe}_2$

- Part 1. MePhSiCl_2 (14.9 g, 0.078 mol) was diluted with ~250 ml of thf. $\text{Me}_4\text{C}_5\text{HLi}$ (10.0 g, 0.078 mol) was slowly added as a solid. The reaction solution was allowed to stir overnight. The solvent was removed via a vacuum to a cold trap held at -196°C . Petroleum ether was added to precipitate out the LiCl . The mixture was filtered through Celite, and the pentane was removed from the filtrate. $\text{MePhSi}(\text{Me}_4\text{C}_5\text{H})\text{Cl}$ (20.8 g, 0.075 mol) was isolated as
- 20 a yellow viscous liquid.

- Part 2. $\text{LiHN}-t\text{-Bu}$ (4.28 g, 0.054 mol) was dissolved in ~100 ml of thf. $\text{MePhSi}(\text{Me}_4\text{C}_5\text{H})\text{Cl}$ (15.0 g, 0.054 mol) was added drop wise. The yellow solution was allowed to stir overnight. The solvent was removed via vacuum. Petroleum ether was added to precipitate out the LiCl . The mixture was filtered through Celite, and the filtrate was evaporated down.
- 30 $\text{MePhSi}(\text{Me}_4\text{C}_5\text{H})(\text{NH}-t\text{-Bu})$ (16.6 g, 0.053 mol) was recovered as an extremely viscous liquid.

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Part 3. $\text{MePhSi}(\text{Me}_4\text{C}_5\text{H})(\text{NH}-i\text{-Bu})$ (16.6 g, 0.053 mol) was diluted with ~100 ml of ether. MeLi (76 ml, 0.106 mol, 1.4 M) was slowly added and the reaction mixture was allowed to stir for ~3 hours. The ether was reduced in volume, and the lithium salt was filtered off and washed with pentane producing 20.0 g of a pale yellow solid formulated as $\text{Li}_2[\text{MePhSi}(\text{Me}_4\text{C}_5)(\text{N}-i\text{-Bu})] \cdot 3/4\text{Et}_2\text{O}$.

Part 4. $\text{Li}_2[\text{MePhSi}(\text{Me}_4\text{C}_5)(\text{N}-i\text{-Bu})] \cdot 3/4\text{Et}_2\text{O}$ (5.00 g, 0.0131 mol) was suspended in ~100 ml of Et_2O . HfCl_4 (4.20 g, 0.0131 mol) was slowly added and the reaction mixture was allowed to stir overnight. The solvent was removed via vacuum and petroleum ether was added to precipitate out the LiCl . The mixture was filtered through Celite. The filtrate was evaporated down to near dryness and filtered off. The off white solid was washed with petroleum ether. $\text{MePhSi}(\text{Me}_4\text{C}_5)(\text{N}-i\text{-Bu})\text{HfCl}_2$ was recovered (3.54 g, 0.0058 mole).

Part 5. $\text{MePhSi}(\text{Me}_4\text{C}_5)(\text{N}-i\text{-Bu})\text{HfMe}_2$ was prepared by adding a stoichiometric amount of MeLi (1.4 M in ether) to $\text{MePhSi}(\text{Me}_4\text{C}_5)(\text{N}-i\text{-Bu})\text{HfCl}_2$ suspended in ether. The white solid could be isolated in near quantitative yield.

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POLYMERIZATIONS

Example 1.

A catalyst solution prepared from 19.7 mg of $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}-t\text{-Bu})\text{ZrMe}_2$ and 6 mg of $[\text{DMAH}][\text{B}(\text{pfp})_4]$ in 20 mls of toluene was added to a 1 liter stainless-steel autoclave containing 400 mls of hexane. The reactor temperature was maintained at 40°C and stirred vigorously while ethylene was added at 90 psi. After 30 minutes the reaction was stopped giving 30 grams of HDPE after work-up. The GPC analysis showed a bimodal distribution with modes centered at 900,000 and 2,000.

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Example 2.

A catalyst solution prepared from 28.6 mg of $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}-t\text{-Bu})\text{ZrMe}_2$ and 9 mg of $[\text{DMAH}][\text{B}(\text{pfp})_4]$ in

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20 mls of toluene was added to a 1 liter stainless-steel autoclave containing 400 mls of hexane. The reactor temperature was set at 50°C and was stirred vigorously while 100 mls of butene and 60 psi of ethylene were added. Following the addition of butene and
5 ethylene, an instantaneous increase in temperature to 90°C was observed. After 30 minutes the reaction was stopped, yielding 130 grams of a waxy ethylene-butene copolymer. GPC analysis showed a bimodal distribution with modes centered at 27,000 and 2,000 in approximately equal ratios. IR spectroscopy showed the presence of
10 butene in the copolymer.

Example 3.

A catalyst solution prepared from 40 mg of $\text{MePhSi}(\text{C}_5\text{Me}_4)(\text{N}-i\text{-Bu})\text{HfMe}_2$ and 11 mg of $[\text{DMAH}][\text{B}(\text{pfp})_4]$ in 20 mls of toluene was added to a 1 liter autoclave containing 400 mls
15 of hexane. The reactor temperature was set at 40°C, stirred vigorously and pressurized with ethylene (90 psi) for 15 minutes. The reactor temperature increased from 40 to 97°C during the polymerization. The reactor was stopped and 98 grams of polyethylene was isolated having a $M_w = 47.7\text{K}$ and a $MWD = 3.0$.

20 Example 4.

A catalyst solution prepared from 50 mg of $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}-i\text{-Bu})\text{ZrMe}_2$ and 68 mg of $[\text{DMAH}][(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}]$ in 20 mls of toluene was added to a 1 liter autoclave containing 400
25 mls of hexane. The reactor temperature was set at 60°C, stirred vigorously and pressurized with ethylene (120 psi) for 60 minutes. The reactor was stopped and 0.44 grams of polyethylene was isolated having a $M_w=538\text{K}$ and a $MWD = 1.90$.

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R-groups are joined forming a C_4-C_{20} ring to give a polycyclic cyclopentadienyl ligand;

(JR_{z-1-y}^1) is a heteroatom ligand in which J is an element in with a coordination number of three from Group V-A or an element with a coordination number of two from Group VI-A of the Periodic Table of Elements, and each R' is, independently a radical selected from a group consisting of C_1-C_{20} hydrocarbyl radicals, substituted C_1-C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, and "z" is the coordination number of the element J;

each Q may be independently, hydride, C_1-C_{20} hydrocarbyl radicals, substituted hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by an electron-withdrawing group such as a halogen atom, or alkoxide radical, or C_1-C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV-A of the Periodic Table of Elements, provided that where any Q is a hydrocarbyl such Q is different from ($C_5H_{5-y-x}R_x$), or both Q together may be an alkylidene, olefin, acetylene or a cyclometallated hydrocarbyl;

"y" is 0 or 1; when "y" is 1, B is a covalent bridging group containing a Group IV A or V A element; "w" is a number from 0 to 3;

and L is a neutral Lewis base; or L represents a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q', wherein M' has the same meaning as M and Q' has the same meaning as Q, as represented by the formula II; and

B. an activator compound comprising
 (1) a cation (with or without a donatable proton)
 and
 (2) a labile, bulky anion which is either a single coordination complex having a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid atom, or an anionic complex containing a plurality of boron atoms, the bulk of said anion being such that upon reaction of the cation of the activator

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compound with a cation reactable substituent of said Group IV-B transition metal so that a Group IV-B metal cation is formed, said anion is sterically hindered from covalently coordinating to the Group IV-B metal cation, and the lability of said anion is such that said anion is displaceable from said Group IV-B metal cation by an unsaturated hydrocarbon having a Lewis base strength equal to or greater than ethylene.

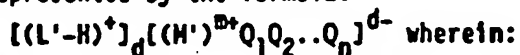
2. The catalyst system of claim 1 wherein the heteroatom ligand group J element is nitrogen, phosphorous, oxygen or sulfur.

3. The catalyst system of claim 2, wherein "y" is 1 and "B" is a linear, branched or cyclic alkylene group having from 1 to 6 carbon atoms, an alkyl substituted silaalkylene group having from 1 to 2 silicon atoms in place of carbon atoms in the bridge, or a Si_1-Si_2 alkyl substituted silanylene group.

4. The catalyst system of claim 3 wherein the heteroatom ligand group J element is nitrogen.

5. The catalyst system of claim 4 wherein "y" is 1 and "B" is an alkyl substituted silaalkylene group having from 1 to 2 silicone carbon atoms in the bridge, or a Si_1-Si_2 alkyl substituted silanylene group.

6. The catalyst system of claim 2, wherein said activator compound is represented by the formula:



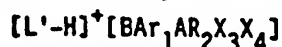
L' is a neutral Lewis base; H is a hydrogen atom; $[L'-H]$ is a Bronsted acid; M' is a metal or metalloid selected from the subtended Groups V-B to V-A of the of the Periodic Table of the Elements; i.e., Groups V-B, BI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A; Q_1 to Q_n are a, independently, hydride, dialkylamido, alkoxide, aryloxy, hydrocarbyl substituted-hydrocarbyl and organometalloid radicals and any one,

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but not more than one of Q_1 to Q_n may be a halide radical; "m" is an integer from 1 to 7; "n" is an integer from 2 to 8; and $n - m = "d"$.

7. The catalyst system of claim 6, wherein said activator compound is represented by the formula:



wherein:

L' is a neutral Lewis base, H is a hydrogen atom, and $[L'-H]^+$ is a Bronsted acid;

wherein:

B is boron in a valence state of three;

Ar_1 and Ar_2 are the same or different aromatic or substituted-aromatic hydrocarbon radicals which radicals may be linked to each other through a stable bridging group; and X_3 and X_4 are independently, a hydride, halide, hydrocarbyl, substituted-hydrocarbyl, or an organometalloid radical.

8. The catalyst of claim 7, wherein said activator compound is represented by the formula:



wherein L' is a neutral Lewis base, H is a hydrogen atom, $[L'H]$ is a Bronsted acid, and B is a boron in a valence of 3+.

9. The catalyst system of claim 7 wherein the heteroatom ligand group J element is nitrogen.

10. The catalyst system of claim 7 wherein M is zirconium.

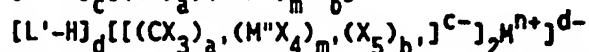
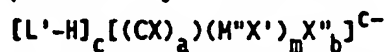
11. The catalyst system of claim 7 wherein the cyclopentadienyl ring group contains four substituent R groups, "x" is 4.

12. The catalyst system of claim 7 wherein M is hafnium.

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13. The catalyst system of claim 7 wherein the cyclopentadienyl group contains one substituent R group, "x" is 1.

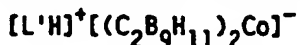
14. The catalyst system of claim 6 wherein said activator compound is represented by the formulae:



wherein $[L'-H]$ is either H^+ , ammonium or a substituted ammonium cation having up to 3 hydrogen atoms replaced with a hydrocarbyl radical containing from 1 to about 20 carbon atoms or a substituted-hydrocarbyl radical, wherein one or more of the hydrogen atoms is replaced by a halogen atom, containing from 1 to about 20 carbon atoms, phosphonium radicals, substituted-phosphonium radicals having up to 3 hydrogen atoms replaced with a hydrocarbyl radical containing from 1 to about 20 carbon atoms or a substituted-hydrocarbyl radical, wherein 1 or more of the hydrogen atoms is replaced by a halogen atom, containing from 1 to about 20 carbon atoms and the like; C is carbon; M'' is boron or phosphorous; each of X, X', X'', X₃, X₄ and X₅ are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals containing from 1 to about 20 carbon atoms, substituted-hydrocarbyl radicals, wherein one or more of the hydrogen atoms is replaced by a halogen atom, containing from 1 to 20 carbon atoms, organometalloid radicals wherein each hydrocarbyl substitution in the organo portion contains from 1 to about 20 carbon atoms and said metal is selected from Group IV-A of the Periodic Table of the Elements and the like; M is a transition metal; "a" and "b" are integers > 0; "c" is an integer > 1; a + b + c = an even-numbered integer from 2 to about 8; and "m" is an integer ranging from 5 to about 22; "a'" and "b'" are the same or a different integer > 0; "c'" is an integer > 2; 'a + b' + c' = an even-numbered integer from about 4 to about 8; "m" is an integer from 6 to about 12; "n" is an integer such that 2c' - n = d; and "d" is an integer greater than or equal to 1.

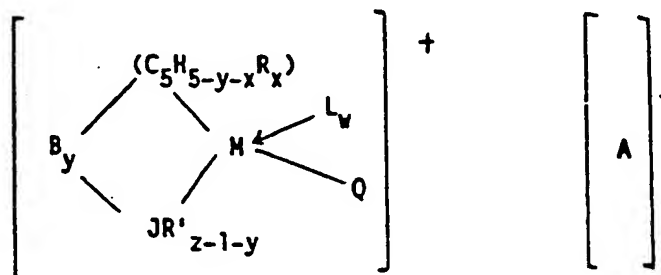
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15. The catalyst of claim 14 wherein the activator component is represented by the following formula:



wherein L' is a neutral Lewis base, H is a hydrogen atom and $[L'H]^+$ is a Bronsted acid.

16. A composition of matter comprising the following general formula:



wherein: M is Zr, Hf or Ti and is in its highest formal oxidation state (+4, d^0 complex);

$(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring which is substituted with from zero to five substituent groups R, "x" is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals, substituted C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, C_1 - C_{20} hydrocarbyl-substituted metalloids wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements, and halogen radicals, or $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming a C_4 - C_{20} ring to give a polycyclic cyclopentadienyl ligand.

(JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group VA or an element with a coordination number of two from Group VI A of the Periodic Table of Elements, and each R' is, independently, a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals,

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substituted C_1-C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, and "z" is the coordination of number of the element J;

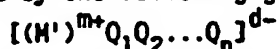
each Q may be independently, hydride, C_1-C_{50} hydrocarbyl radicals, substituted hydrocarbyl radicals wherein one or more hydrogen atom is replaced by an electron-withdrawing group such as a halogen atom, or alkoxide radical, or C_1-C_{50} hydrocarbyl-substituted metalloids wherein the metalloid is selected from the Group IV-A of the Periodic Table of Elements, provided that where any Q is a hydrocarbyl such Q is different from $(C_5H_5-y-xR_x)$, or both Q together may be an alkylidene, olefin, acetylene or a cyclometallated hydrocarbyl.

"y" is 0 or 1; when "y" is 1, B is a covalent bridging group containing a Group IV A or V A element.

L is a neutral Lewis base; and "w" is a number from 0 to 3.

$[A]^-$ is a labile bulk anion which is either a single coordination complex having a plurality of lipophilic radical covalently coordinated to and shielding a charge bearing metal or metalloid center or an anionic complex containing a plurality of boron atoms.

17. The composition of matter of claim 16 wherein $[A]^-$ is represented by the following general formula



wherein M' is a metal or metalloid selected from the Groups subtended by Groups V-B to V-A of the Periodic Table of the Elements; i.e., Groups V-B, VI-B, VII-B, VIII, I-B, II-B, III-A, IV-A, and V-A;

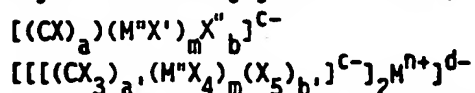
Q_1 to Q_n are selected, independently, from the Group consisting of hydride radicals, dialkylamido radicals, alkoxide and aryloxy radicals, hydrocarbyl and substituted-hydrocarbyl radicals and organometalloid radicals and any one, but not more than one, of Q_1 to Q_n may be a halide radical, the remaining Q_1 to Q_n being, independently, selected from the foregoing radicals;

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m is an integer from 1 to 7;

n is an integer from 2 to 8; and $n - m = d$.

18. The composition of matter of claim 16 wherein $[A]^-$ is represented by the following general formula:

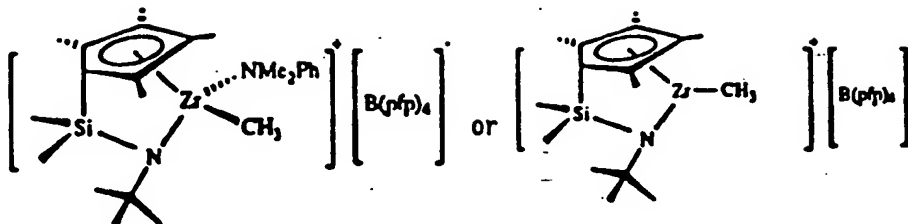


C is carbon; M^m is boron or phosphorous; each of X, X', X'', X₃, X₄ and X₅ are radicals selected, independently, from the group consisting of hydride radicals, halide radicals, hydrocarbyl radicals containing from 1 to about 20 carbon atoms, substituted-hydrocarbyl radicals, wherein one or more of the hydrogen atoms is replaced by a halogen atom, containing from 1 to 20 carbon atoms, organometalloid radicals wherein each hydrocarbyl substitution in the organo portion contains from 1 to about 20 carbon atoms and said metal is selected from Group IV-A of the Periodic Table of the Elements and the like; M is a transition metal; "a" and "b" are integers > 0; "x" is an integer > 1; a + b + c = an even-numbered integer from 2 to about 8; and "m" is an integer ranging from 5 to about 22; "a'" and "b'" are the same or a different integer > 0; "c'" is an integer > 2; a' + b' + c' = an even-numbered integer from about 4 to about 8; "m'" is an integer from 6 to about 12; "n" is an integer such that 2c' - n = d; and "d" is an integer greater than or equal to 1.

19. The composition of matter of claim 17 wherein $[A]^-$ is $B(C_6F_5)_4^-$.

20. The composition of matter of claim 18 wherein $[A]^-$ is $[(C_2B_9H_{11})_2Co]^-$.

21. A composition of matter of formula



22. A method of producing a catalyst system of claim 1 which comprises admixing the Group IV-B transition metal component A and the activator compound B to form the desired catalyst system.

23. A catalyst system according to claim 1 or a method according to claim 22 wherein A and B are in a molar ratio of from 1:1 to 200:1.

24. A process for producing a homo- or co-polyolefin which comprises (co)polymerizing one or more olefinically unsaturated monomer(s) in the presence of a catalyst system according to any of claims 1 to 15 and 23 or a composition of matter according to any of claims 16 to 21.

25. A process according to claim 24 when performed in the liquid phase.

26. A process according to claim 24 or 25 wherein the catalyst system or composition of matter is introduced into the monomers per se or is formed in situ in the polymerization mixture.

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